

# UNPUBLISHED PRELIMINARY DATA

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## ABSTRACT

The quenched-in resistivity of a dilute alloy is analyzed in terms of the contributions caused by vacancies and by changes in the short-range order. It is shown that the vacancy contribution varies in a linear fashion with solute concentration and the short-range order term as the square of the solute concentration. Depending on the temperature, concentration and controlling physical parameters, either effect can predominate. The vacancy dependence on solute concentration is determined by the solute-vacancy interaction energy which can be evaluated from theory. The short-range order term depends on the solute vacancy interaction and on the difference in resistivity increment between an isolated solute atom and a paired solute atom. Both these quantities may be positive or negative leading to the explanation of a negative quenched-in resistivity which has been observed in the present work in the Au-Ag system and in the Au-In system.

## OTS PRICE

XEROX

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\$



## QUENCHED-IN RESISTIVITY IN DILUTE ALLOYS

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### INTRODUCTION

In a dilute alloy the resistivity changes on quenching are considerably more difficult to analyze than those in pure metals. In addition to the resistivity increase due to the quenched-in vacancies; there is also, as Korevaar<sup>1</sup> has pointed out, a contribution due to changes in the short-range order with temperature. It is attempted here to derive a simple expression predicting the change in resistivity for dilute alloys which takes into account both effects. This expression should be valid in the limiting case of very rapid quenching rates and alloys sufficiently dilute so that solute complexes containing more than two atoms can be neglected.

With the normal cooling rates achieved in quenching experiments it is well known that there may be a significant loss of vacancies during the quench especially at temperatures approaching the melting point<sup>2</sup>. In dilute alloys, analysis of the vacancy loss is difficult because the average jump frequency of a vacancy or divacancy is a rather complicated function of temperature<sup>3</sup>. In addition, there are changes in the short-range order that will take place during the quench<sup>4</sup>. Fortunately, since it now appears that the resistivity increment caused by associated defects is very nearly the same as the sum of the individual contributions<sup>5</sup> it is not necessary to know how many of the vacancies are associated with solute atoms or what fraction occur as divacancies.

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## THEORY

For simplicity we will assume that no vacancies are lost during the quench and further that there is no change in the short-range order.\* As Lomer<sup>6</sup> and more recently Lidiard<sup>7</sup> has shown the concentration of vacancies  $n_v$  in a dilute alloy is given by

$$n_v = \{ 1 + zc [ \exp (-\Delta g/kT) - 1 ] \} \exp (-g/kT) \quad 1$$

where  $z$  is the coordination number,  $c$  is the solute concentration,  $g$  is the free energy of vacancy formation in the pure solvent and  $g + \Delta g$  is the vacancy formation free energy with one solute atom as nearest neighbor. If  $\rho_v$  is the resistivity increment per unit vacancy concentration irrespective of nearest neighbors, then the vacancy contribution to the quenched-in resistivity  $\Delta\rho_v$  is simply

$$\Delta\rho_v = \rho_v n_v \quad 2$$

We consider now the effects of short-range order on resistivity. This problem has been previously analyzed by Gibson<sup>8</sup> who used the results of his analysis to consider the resistivity changes in disordered  $\text{Cu}_3\text{Au}$ . In the present situation, since we are concerned only with dilute alloys a simpler formulation is possible. For a dilute alloy, the short-range order parameter  $\alpha$  is small and we may write<sup>9</sup>

$$\alpha = c(1-c) [ \exp(2\mu/kT) - 1 ] \quad 3$$

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Even though it follows from the Flynn analysis that the resistivity increment of a solute pair of atoms differs by only a few per cent from that of the isolated atoms, this change cannot be neglected since the dilute alloy may very well have at least a hundred times greater solute concentration than vacancy concentration.

where  $\mu$  is the interaction energy (one-half the energy required to form 2 A-B bonds from one A-A bond and one B-B bond). From equa. 3 it follows that for a dilute alloy the number of isolated solute atoms is

$$n_I = c [ 1 - zc \exp (2\mu/kT) ] \quad 4$$

The difference between the concentration of isolated solute atoms after quenching and after complete annealing is then

$$\Delta n_I = -zc^2 [ \exp(2\mu/kT_q) - \exp(2\mu/kT_o) ] \quad 5$$

where  $T_q$  is the quenching temperature and  $T_o$  is the temperature at which the alloy comes to thermal equilibrium on slow cooling after annealing. If we let  $\rho_I$  be the resistivity increment per mole caused by isolated solute atoms and  $\rho_{II}$  be one-half the increment per mole of solute pairs then the resistivity change due to short-range ordering is\*

$$\Delta \rho_{SRO} = (\rho_I - \rho_{II}) \Delta n_I \quad 6$$

The total quenched-in resistivity  $\rho_T$  is then

$$\begin{aligned} \Delta \rho_T = n_v \{ & 1 + zc[\exp(-\Delta g/kT)-1] \} \\ & - (\rho_I - \rho_{II}) zc^2 [\exp(2\mu/kT_q) - \exp(2\mu/kT_o)] \end{aligned} \quad 7$$

#### EXPERIMENT AND DISCUSSION

If we assume that  $(\rho_I - \rho_{II}) > 0$  then for an alloy with a tendency for ordering  $\mu$  is negative the SRO contribution to the quenched-in resistivity is negative. A negative quenched-in resistivity has in fact been observed by Hamaguchi<sup>10</sup> for Au-Pd alloys, by Korevaar<sup>1</sup> for a Au-Cu alloy and in the present investi-

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\*Note that with this model the resistivity maximum occurs at complete SRO or complete clustering depending on whether  $(\rho_I - \rho_{II}) > 0$  or  $(\rho_I - \rho_{II}) < 0$ . For  $\text{Cu}_3\text{Au}$  above the critical temperature for long range order, Damask<sup>11</sup> has found that the resistivity does in fact decrease with decreasing SRO.

gation for Au-Ag alloys and in Au-In alloys\*. If  $\Delta g$  is negative indicating an attraction between solute atoms and vacancies we then expect that at high temperatures the vacancy contribution to  $\Delta\rho_T$  will increase linearly with  $c$  while the S.R.O. contribution will lead to a parabolic decrease. At low quenching temperatures, say below 500°C for Au, the vacancy contribution is very small so that one should observe only the S.R.O. effect. For a single dilute alloy specimen then the following behavior is expected with increasing quench temperature: initially an increasing negative quenched-in resistivity with increasing temperature followed by a resistivity minimum and then at sufficiently high temperatures an increasing positive quenched-in resistivity. This is precisely the result that has been observed by Korevaar and Hamaguchi and in the present investigation. A typical result for a Au-3At.%Ag alloy is shown in Fig. 1.

Neglecting entropy changes, the quantity  $\Delta g$  can be calculated by means of the work of Flynn<sup>13</sup> or Le Claire<sup>2</sup> as a function of valence difference between solute and solvent. If size effects predominate, the analysis of Swalin<sup>14</sup> can be used. In some systems

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\*Hamaguchi interpreted his results in terms of a negative resistivity increment for a solute-vacancy pair, which seems unlikely in view of the Flynn analysis. Logie et al<sup>12</sup> have studied the effect of plastic tensile strains on Au-Pd alloys and found that over a wide range of compositions there is a decrease in resistivity on plastic deformation. This is in agreement with the work of Hamaguchi since plastic working decreases the amount of local order and thus should decrease the resistivity. Logie apparently rejected this sort of argument on the basis that there is no long-range ordering in the Au-Pd system. This does not appear to be a sufficient reason since, in the Au-Ag system there is certainly no long range order and it is shown in the present paper that changes in the short-range order are sufficient to explain the resistivity changes. A more complete analysis of the Logie data is in progress.

$\mu$  has been determined experimentally, and  $n_V \exp(-g/kT)$  is known from quenching experiments on the pure metal.  $(\rho_I - \rho_{II})$  is not known with precision but from experimental data available for  $\rho_I$ <sup>15</sup> and using the results of Flynn<sup>5</sup> an upper limit can be obtained.

To check the present analysis Au-Ag specimens containing up to 3 At. % Ag and Au-In specimens containing up to 3 At. % In were prepared. The specimens were in the form of wires 0.01 inch diameter wound on a quartz frame for support. Heating was accomplished in a vertical tube furnace filled with purified He. At the bottom of the furnace was a refrigerated brine solution at -20°C into which the specimens were quenched. Resistance measurements were made on the specimens in a liquid nitrogen bath immediately after quenching and then after annealing. Annealing was accomplished by passing a sufficient current through the specimen to heat it to about 500°C.

For low quenching temperatures the results followed the theory within experimental error. The accuracy of this sort of experiment is not very great at low quench temperatures because of the small resistance changes and because results on many different specimens must be compared. For the Au-Ag alloys all the parameters of equa. 7 are known except  $\rho_{II}$  and  $T_0$ . From the work of Norman<sup>16</sup>  $\mu = -.007$  ev,  $\rho_I = .38 \times 10^{-4}$  ohm cm/at. fraction Ag from Linde's work<sup>15</sup>,  $T_0$  was taken as 300°K,  $n_V \exp(-g/kT)$  was taken from the present work and  $\Delta g$  was taken as zero in agreement with previous experimental work<sup>17</sup> and theory. It is seen in Fig. 2 that the experimental data are reasonably well fitted by the theoretical curve

if  $(\rho_I - \rho_{II})$  is taken as  $0.01 \rho_I$ . The coefficient .01 agrees well with what might be expected from the Flynn theory. The data for the Au-In alloys show also an increasing negative quenched-in resistivity with increasing solute concentration as seen in Fig. 3. From the Au-In equilibrium diagram it might be anticipated that dilute alloys would show short-range ordering as appears to be the case. Since no data are available for  $\mu$  in this system it is not possible to compare these results with theory.

High temperature results for both systems did not fit the theory. It is believed the reason for this has to do with the large changes that take place during quench for high quenching temperatures. A complicating feature to this problem is that the thermal conductivity decreases with increasing alloy content so the quenching rate decreases sharply. For pure Au the quenching rate was  $35,000^\circ\text{C}/\text{sec}$ . whereas for a 1.5% In alloy the rate dropped to  $12,000^\circ\text{C}/\text{sec}$ . Work is presently in progress to increase the quenching rates and take into account the changes occurring during the quench.

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CAPTIONS FOR FIGURES

- Figure 1. Quenched-in Resistivity versus Quench Temperature for a Au 3 At% Ag Specimen.
- Figure 2. Quenched-in Resistivity as a Function of Ag Concentration in At%. The solid curves are based on Equn. 7 Taking  $e_I - e_D$  as .01  $e_I$ ,  $u$  as -.007  $T$ , as 300°K, and  $Ag$  as 0.
- Figure 3. Quenched-in Resistivity as a Function of  $I_n$  Concentration in At.%. The qualitative behavior is similar to that observed in the Au-Ag system.

OHM-CM  
X10<sup>8</sup>

QUENCHED-IN RESISTIVITY  
Au - 3%Ag



